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16. ABSTRACT

An automated system has been designed and operated successfully for the past two years for chemical analysis of nitrogen, phosphorus, and carbon compounds in the study of the fate of pollutants. Nine samples from along a simulated river are pumped into the laboratory, and eight different chemical analyses are done on each sample in a consecutive and automated mode with built-in internal standardization. The samples are directed by a series of solenoid valves, which are activated by either a mechanical or a solid state sequencer. The analyses are done with Technicon autoanalyzers in a continuous flow mode, and data processing is performed by a computer linked to the system.

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By Heinz P. Kollig

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JOURNAL ARTICLE

An automated multisample-stream chemical monitoring system

A KNOWLEDGE OF the distribution of nutrients in aquatic ecosystems is of great importance to the understanding of microbial behavior in the study of the fate of aquatic pollutants. Experimental systems ranging from small-scale microcosms to large systems simulators are being found useful in research on environmental problems. One difficulty encountered in operating any such system is obtaining necessary measurements. For larger aquatic systems, for example, one might wish to obtain time series measurements of such items as those listed in *Table 1*. An automated system for obtaining such measurements from a flowing system is presented and might prove valuable to other research efforts using medium- to large-scale aquatic microcosms or simulators.

Table 1

Parameters to be measured in AEcoS experiments

Total Kjeldahl nitrogen
Ammonia
Nitrite
Nitrate
Total phosphorus
Orthophosphate
Chemical oxygen demand
Glucose

Mr. Kollig is Research Chemist, Environmental Research Laboratory, U.S. Environmental Protection Agency.

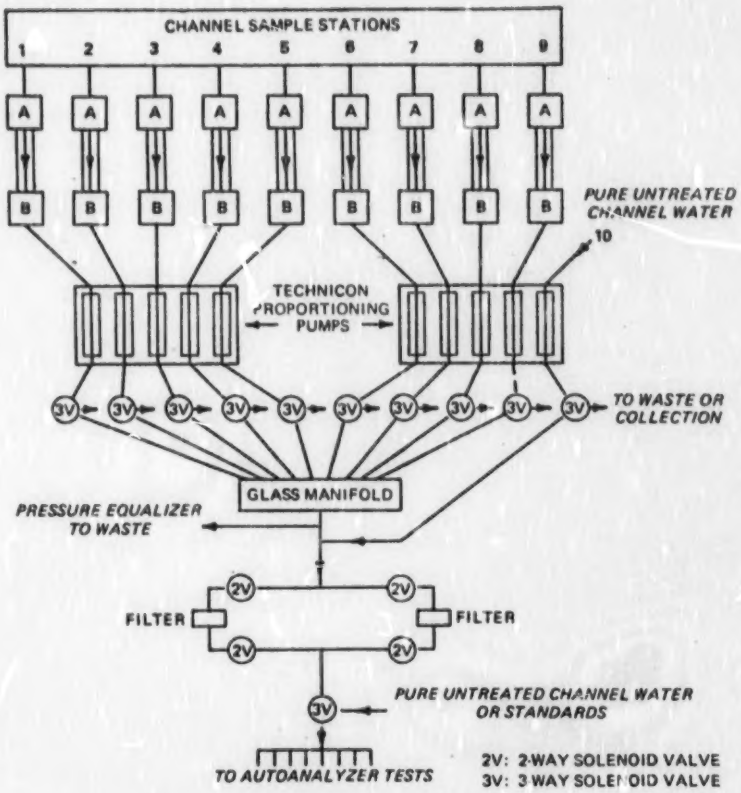

Figure 1 *Flow diagram of entire sampling system.*

Such studies are performed at the U.S. EPA Environmental Research Laboratory, Athens, Georgia, in the Aquatic Ecosystem Simulator (AEcoS).[1] The AEcoS is an artificial, controlled aquatic system containing a flow channel 19.5 m long, 46 cm wide,

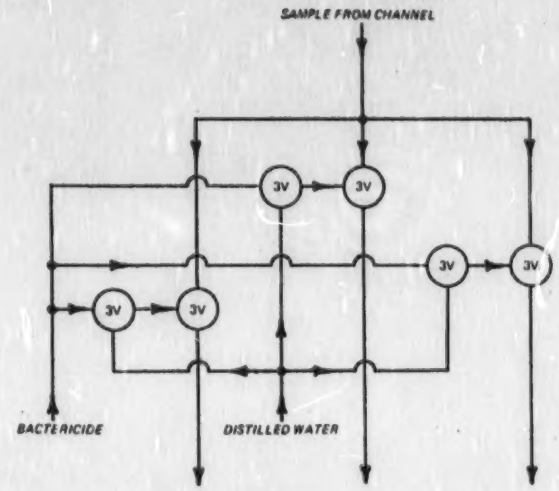

Figure 2 *Detailed view of solenoid valve system A.*

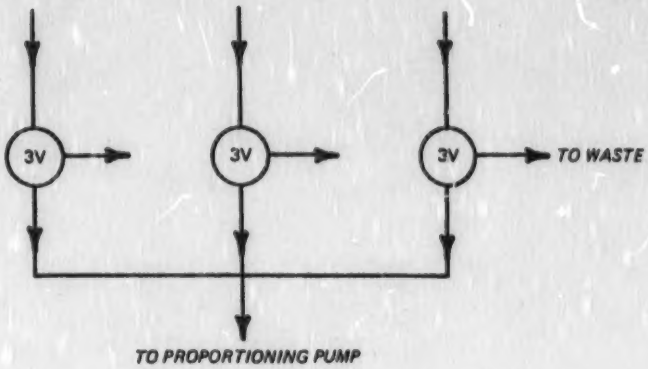

Figure 3 *Detailed view of solenoid valve system B.*

and 46 cm deep. Nine sampling stations are located at 2.4-m intervals for chemical characterization of the water. Water used in channel experiments is first deionized, and then distilled. The water is then treated by adding known amounts of nutrients and pollutants to be studied.

To determine the nutrient distribution, the chemical characterization at each sampling point should include evaluation of the parameters listed in Table 1. An automatic sampling and analysis system was therefore developed which allows these materials to be measured dynamically at each of the nine sampling locations.

The system

The entire system is depicted in the flow diagram of *Figure 1*. *Figures 2* and *3* show detailed views of the solenoid valve systems A and B (Automatic Switch Co.)

Three 3-mm polytetrafluoroethylene (PTFE) tubing lines are fed into a solenoid valve system (A) at each sampling station: one from the channel stream, one from a bactericide cleaning solution, and one from a distilled water source. The three solutions exit from the solenoid system (A) via three 3-mm PTFE tubing lines. The valve system rotates the three input solutions among the three output lines at predetermined intervals so that each output line carries channel sample, bactericide solution, and distilled water sequentially. The three output lines from A are guided through an insulated 10-cm PVC pipe that is cooled to 4°C by a circulating 10% antifreeze solution.

Each of the three lines from A leads to a three-way solenoid valve at B. At any given moment the valve for the line that carries the sample is open (Figure 1) to permit flow through the system, whereas the lines with bactericide and distilled water are diverted to waste. The opening and closing of valves at B are coordinated with the rotational switching at A. The samples flow from B through the pumps to individual three-way solenoid valves. Only one of these is open at a time to permit flow through the system. The other eight samples may be collected for additional tests or may flow to waste. The sample that continues flows through a glass manifold to a tee connection, which directs the sample in one of two directions, depending on which pathway is open. Each pathway leads through a set of two-way valves and a bacterial

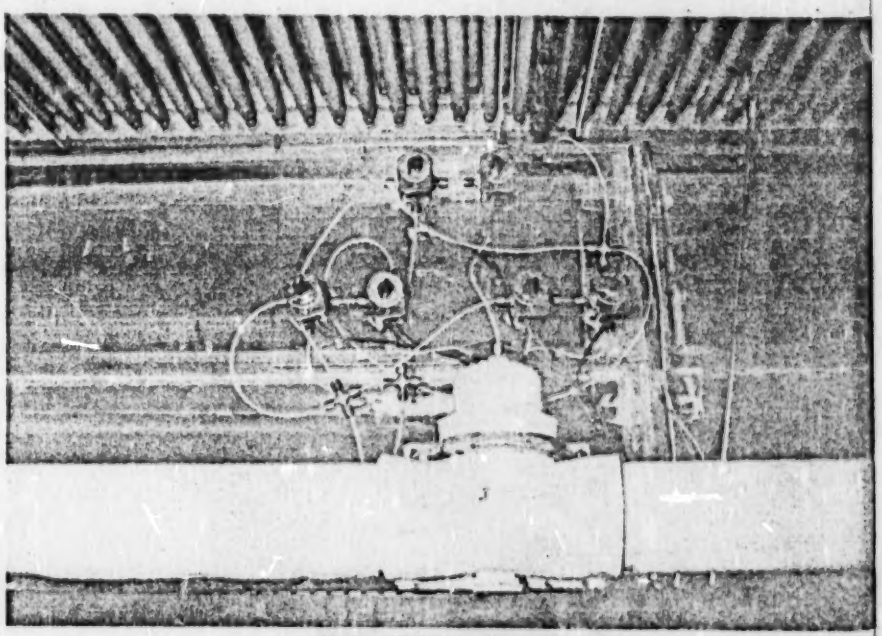

Figure 4 *Solenoid valve setup A.*

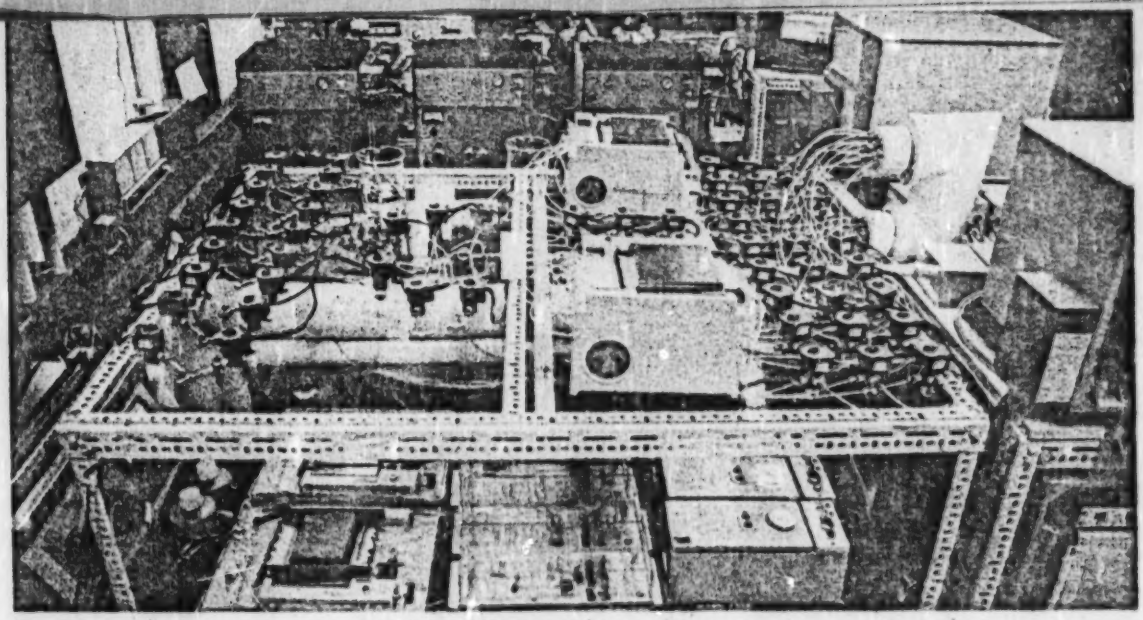

Figure 5 *Continuation in laboratory with all 27 PTFE sample lines emerging from cooling pipe and leading to solenoid valves of B.*

filter, through a last three-way solenoid valve, and into a sample splitter (Technicon). The number of portions into which the sample is divided is determined by the number of tests to be carried out.

Figure 4 shows the solenoid valve setup of A, and *Figure 5* shows the continuation in the laboratory with all 27 PTFE sample lines emerging from the cooling pipe and leading to the solenoid valves of B.

Standardization is achieved by by-passing the entire sample system. Pure untreated channel water (used to establish the baseline) and standards are fed through the last solenoid valve before the sample splitter. A tenth sample station is provided to feed pure untreated channel water for internal standardization.

The coordinated switching of the individual solenoid valves is performed by a custom-made cam-operated sequencer (obtained from Bill Fincher and Associates). The mode of sequencing is such that each of the nine samples plus the tenth sample taken (untreated channel water) is analyzed for 3 min with a cycle duration of 30 min. The sample-station and cleaning rotation among the three lines of each sample station between valve systems A and B occurs every 30 min also (including the tenth simulated sample station). This switching, however, cannot be done simultaneously at all nine sample stations, because a certain length of time is required for each sample slug to travel from the channel to the analyzer, and only one sample at a time can be analyzed. Each sample has distilled water in front and is followed by cleaning solution. Since the analysis of the nine samples plus the internal standard is staggered over 30 min, the sample rotation is staggered accordingly from station to station so that the 3 min of sample comes from approximately the center of the sample slug. An alternative to the mechanical sequencer is one built from electronic solid-state devices that performs in a more precise manner and permits easier changes in timing.

Discussion

The bactericide used for cleaning the sample lines of bacterial growth is a solution of 5 mg of chlorine/l of water, prepared from commercial bleach. It is pumped through the sample lines from a separate container, as is the distilled water. (The pumps were obtained from Fluid Metering, Inc.) Cleaning and cooling of sample lines has been very effective in preventing blockage by bacterial growth over 2 yr of operation.

The lengths of the sample lines in our system vary from 15-30 m. Since it is desirable to have all samples stay in the lines the same length of time, an adjustment can be made at the pump by installing different sizes of pump tubes. The time the sample travels through the manifold cartridge (Technicon) to the colorimeter is also different from test to test and can be adjusted by adding different lengths of glass coils to each test manifold. The output of each colorimeter is connected to a PDP-8 computer, programmed to take a reading of all tests at 3-min intervals. Each sample must therefore flow through all colorimeters at the same time. The glass manifold is a strip of capillary tubing (10-mm o.d. × 3-mm i.d.) to which 10 connections are fused.

The bacterial filtering is done with a 25-mm filter holder (Swinnex) using a 0.5-μm fluorocarbon membrane filter (Millipore Corp.) One filter holder is mounted between each set of two-way solenoid valves (Figure 1). When one filter is completely exhausted, the sample flow is directed to the other. A new filtering system is under investigation that will filter each sample individually and automatically. However, in the concentration ranges run in this laboratory, most tests are not affected by a bacterial concentration of up to 10^4/ml, omitting the

filter. This bacterial concentration has been found to interfere with the glucose test by giving an equivalent glucose concentration of 0.2 mg/l.

Since the mode of sampling is a continuous one, there are no peaks as with discrete sampling. Standardization is performed in a continous mode by aspirating standards manually into the last solenoid valve before the sample splitter. A standard solution is prepared to contain all chemical species of interest. Once the "window" of the AutoAnalyzer™ II (Technicon) is set, i.e., 0% and 100%, it does not change, even if a baseline drift occurs. This property has been utilized by adding a tenth sampling station that draws pure untreated channel water instead of sample. Each sample is analyzed for 3 min. At the tenth station, channel water used during standardization to establish the baseline is analyzed. This serves two purposes. First, any drift can be readily observed and corrected. Second, since the size of the window does not change, running pure water accomplishes the same purpose as running standards. An automatic internal standardization has been achieved that standardizes the system once every cycle. If a drift of baseline occurs, the adjustment has to be made manually by an operator. However, investigations are being undertaken to automate this also.

The performance of the system is checked periodically by dipping samples out of the channel in beakers, by-passing the sampling part of the system, and running them straight through the AutoAnalyzers. A comparison of these samples with those run through the entire system indicates only slight differences between them. However, since most of the chemical species experience a concentration gradient along the channel during an experiment, one should expect slight differences in concentrations in samples taken from about the same area in a dynamic system. By-passing the sampling part of the system will also indicate any adsorption or diffusion of chemical species onto or through the PTFE sample tubing. At the low concentration range, the orthophosphate concentration has been found to decrease by about 15% running through the entire system rather than by-passing the sampling part.

A statistical evaluation of the system was obtained by substituting standards for channel water samples at each sampling station. This was accomplished by pulling all glass sampling probes out of the channel and dipping each into a beaker containing all chemical species of interest, each beaker containing a different concentration. *Table 2* lists the tests for which statistical data were calculated at their corresponding concentration levels. These tests have a detection limit of 0.001 mg/l except the glucose test, which has a detection limit of 0.01 mg/l. Performing analyses at these low ranges requires a setting of maximum sensitivity in the colorimeter and changes in the reagent/sample ratios in the manifold assembly.

Conclusion

The chemical analytical system described is fully automated and computerized for the analysis of eight parameters on nine independent samples. However, it is practically unlimited in the number of samples that may be analyzed, and the number of tests that may be carried out depends only on the volume of sample that can be pumped into the laboratory. The cooling and frequent automatic cleanup of sample lines keep the system from clogging with bacterial growth. The system should provide a basis for models for other applications.

Reference

1. SANDERS, W.M. and FALCO, J.W., in *Advances in Water Pollution Research* (Pergamon Press, New York, 1973) pp. 243-253.

Table 2

Statistical evaluation of the system[a]

Test	Conc., mg/l	Std. dev.	Std. error of mean	Coefficient of variation, %
Nitrate-N	0.050	0.0011	0.00043	2.5
	0.250	0.0026	0.00099	1.2
Nitrite-N	0.010	0.00068	0.00026	6.2
	0.050	0.00021	0.000078	0.4
Ammonia-N	0.050	0.00095	0.00036	1.8
	0.250	0.0027	0.0010	0.9
o-Phosphate-P	0.050	0.0039	0.0015	10.5
	0.250	0.0051	0.0019	2.3
Glucose	1.00	0.016	0.0062	1.6
	5.00	0.034	0.013	0.7

[a] Number of sample points = 7.